

Surfactant Adsorption in Gas Hydrate Systems

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Clathrate hydrates are molecular inclusion compounds, where molecular cages of water encapsulate lighter organic species (e.g., methane), typically at high pressure and low temperature. Using an advanced micromechanical force apparatus, we have measured the cohesive force between cyclopentane hydrate particles suspended in a hydrocarbon bulk phase containing a variety of carboxylic acids. Acting as surfactants, these acids decreased the water-oil interfacial tension and reduced the strength of the capillary bridge between hydrate particles. Based on fundamental knowledge of capillary cohesion, we hypothesize that polynuclear aromatic carboxylic acids alter the wettability of the hydrate surface, further reducing cohesive force. To investigate surfactant adsorption in hydrate systems, we compare direct measurements of oil-air surface tension, oil-water interfacial tension, and hydrate cohesive force as a function of surfactant concentration. The results show agreeable interfacial adsorption trends in oil+air and oil+water systems. When a hydrate phase is present, surfactant adsorption begins at lower concentrations (3-4 orders of magnitude lower than in non-hydrate systems). To better quantify these trends in interfacial activity, we have utilized baseline cohesive force measurements (without surfactant) to estimate the surface free energy of cyclopentane hydrate, which is hypothesized to be at least one order of magnitude below that of stainless steel. To our knowledge of the literature, these results represent the first investigation to quantify the impact of a hydrate phase on surfactant adsorption.